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Chapter

Recycling Polymeric Materials for Corrosion Control

Mohamed A. Deyab

Abstract

The purpose of this chapter is to present the state of the art for using recycled polymeric materials as effective corrosion inhibitors for metals in different corrosive solutions. Initially, the chapter provides the information about corrosion definition, rust formation, and corrosion costs. The chapter gives comprehensive picture about the standard practices for corrosion control, highlighting the recent trends. In addition, it summarizes the corrosion inhibition mechanism in different media. Recent and novel corrosion inhibitors based on recycling several polymeric materials are reviewed and are presented according to the area of application of the inhibitors. As presented, recent trends are focusing on the compounds that are environmentally friendly and less toxic to the environment.

Keywords: recycling polymeric materials, corrosion inhibitors, corrosive solutions, metals

1. Introduction

1.1 Definition of corrosion

Corrosion is a spontaneous process, which transforms a polished metal to a more chemically-stable form (e.g., oxide, hydroxide, or sulfide). It is the gradual destruction of metals by chemical and/or electrochemical reaction with their environment [1–4].
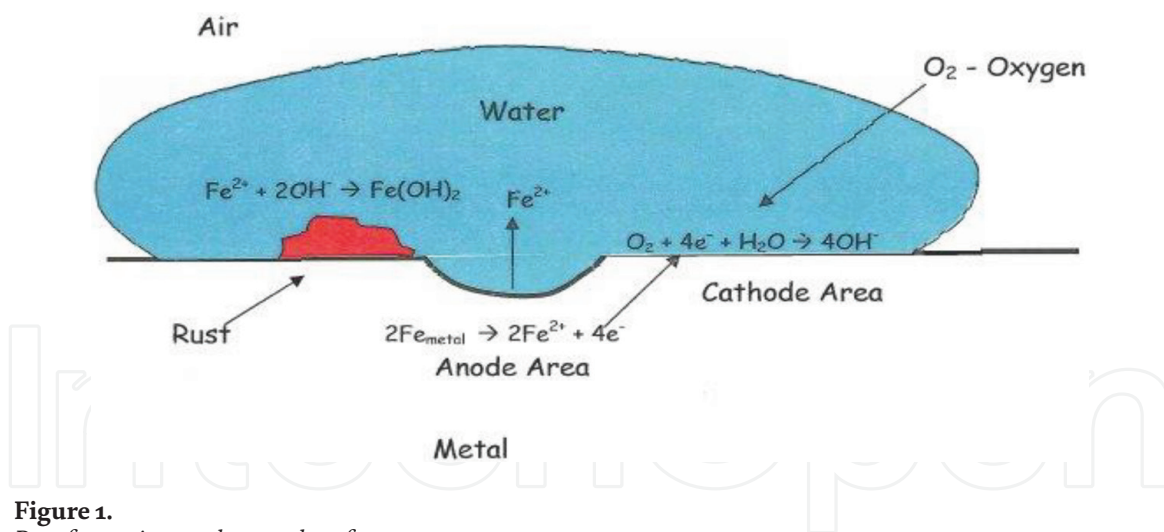
Corrosion has an effect on the microstructure, mechanical features and the physical aspect of the materials. Rusting and other types of deterioration drastically reduce the capacity of pipelines and equipment, resulting in loss of output as well as loss of equipment, or even life.

1.2 Rust formation

Rust is a generic term [5] to describe a series of different oxides, $Fe(OH)_2$, $Fe(OH)_3$, $FeO(OH)$, $Fe_2O_3 \cdot H_2O$ that form when iron corrodes. The common form of rust is a red product Fe_2O_3 called hematite (**Figure 1**).

1.3 Corrosion costs

According to the recent reports issued by international NACE organization, the global cost of corrosion to be US$2.5 trillion. This cost equivalent to roughly 3.4% of the global gross domestic product (GDP) [6].

Figure 1.
Rust formation on the metal surface.

1.4 Corrosion control

The corrosion control in different industrial fields can be controlled by the following strategy. They include [7]:

1. Protective coatings

2. Cathodic protection

3. Materials selection

4. Corrosion inhibitors

Protective coatings are effective tools for controlling the corrosion hazards [8–10]. These substances are often applied in conjunction with cathodic protection systems to provide the most cost-effective protection for a structure [11–14].

Cathodic protection (CP) is a technology that uses direct electrical current to stop the corrosion. It is an effective method for underground petroleum storage tank or natural gas pipeline. On new systems, CP can control the corrosion from starting; on existing systems; CP stop the existing corrosion from getting worse.

Materials selection refers to the use of highly corrosion resistant materials such as stainless steels, to enhance the life time of metal systems [15, 16].

Corrosion inhibitors are chemicals compounds that added by small quantities to a particular corrosive media, to overcome on the corrosive hazards of surrounding corrosive media [17–21].

2. Recycling polymeric materials as effective corrosion inhibitors

The recycling of polymeric waste and use of their modified products as effective corrosion inhibitors for metal corrosion are limited [22]. In this section, it is intended to report a series of efforts aimed to the converting plastic waste into useful material used to control the corrosion of metal in very high corrosive environmental.

2.1 Recycling polyethylene terephthalate (PET) plastic waste as corrosion inhibitors

Nowadays, PET plastic show the unique marketing and lifestyle advantages [23–25]. The chemical nature of PET plastic allows to easy recyclability by various recycling methods. Recycling of PET has become an important way from the environmental point of view and it has given commercial opportunity due to wide spread use and availability of PET bottles, packages and fibers [26, 27].
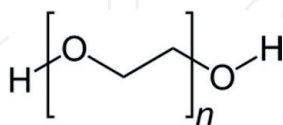
Abdel Hameed et al. [28] prepare some of corrosion inhibitors derived from PET plastic waste. These PET plastic wastes were used to inhibit the corrosion carbon steel in acid corrosive media [29].

Abd El Hameed et al. [22] were prepared new corrosion inhibitors based on the modify (PET), with di-ethanolamine (DEA) and tri-ethanolamine (TEA) using manganese acetate as a catalyst. The prepared corrosion inhibitors were used to protect the carbon steel which used in the manufacture of petroleum pipelines in nitric acid, at different concentrations of inhibitors from 50 to 250 ppm and different temperatures, ranged from 303 to 333 K.

Ayman et al. [30], prepared water soluble corrosion inhibitor from recycled PET. In this work, PET was de-polymerized by TEA into glycolyzed product, followed by esterification with bromoacetic acid in the presence of manganese acetate as a catalyst. The prepared compound was used as corrosion inhibitor for XL65 carbon steel, in 2 M HCl solution. The effectiveness of recycled PET corrosion inhibitor was confirmed by various electrochemical techniques such as open circuit potential, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The results of these investigations showed enhancement in inhibition efficiencies with the increasing of inhibitor concentration.
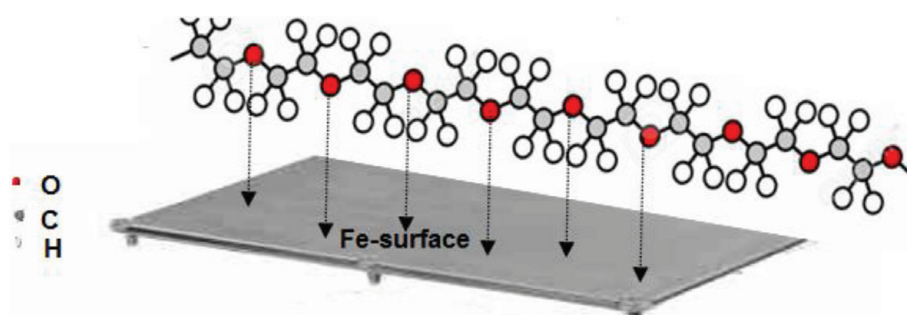
2.2 Recycling poly(ethylene glycol) as corrosion inhibitors

Poly(ethylene glycol) (PEG) is a polyether compound with many applications from industrial manufacturing to medicine [31]. Poly(ethylene glycol) (PEG) is also known as polyethylene oxide (PEO) or polyoxyethylene (POE), depending on its molecular weight. The structure of PEG is commonly expressed as $H—(O—CH_2—CH_2)_n—OH$.

High-molecular weight PEG is synthesized by suspension polymerization of waste materials [32]. It is necessary to hold the growing polymer chain in solution in the course of the poly-condensation process. The reaction is catalyzed by magnesium, aluminum, or calcium-organo-element compounds. To prevent coagulation of polymer chains from solution, chelating additives such as dimethylglyoxime are used.

The use of PEG as corrosion inhibitors was investigated by Deyab and Abd El-Rehim [33]. They studied the effect of PEG of various average molecular weights (MW = 1200, 4000 and 6000) as inhibitors for the corrosion of carbon steel in 1.0 M butyric acid. They found that the corrosion rate of carbon steel in butyric acid decreased with increasing PEG concentration and molecular weight and increased with increasing temperature. PEG inhibits the corrosion of carbon steel by an adsorption mechanism.

Figure 2.
Showing how a PEG polymer protects the metal from corrosion.

These polymers inhibit the acid dissolution of carbon steel by adsorption at the Fe/acid solution interface. The adsorption process takes place via ion pair and ion exchange mechanism by their ethylene oxide groups [34]. **Figure 2** showing how a PEG polymer protects the metal from corrosion. Inhibition of the PEG can be explained by a substitution adsorption of the polymers according to the following equation.

$$\text{Polymer}_{(aq)} + x\text{H}_2\text{O}_{(ads)} = \text{Polymer}_{(ads)} + x\text{H}_2\text{O}_{(aq)} \tag{1}$$

The data imply that the PEG(6000) has higher corrosion inhibition than PEG(4000) and PEG(1200), indicating that the corrosion inhibition of these polymer increases with the increase in their molecule weights. This is due to the increase in the number of ethylene oxide group [($-\text{CH}_2\text{OCH}_2-$)n] with an increase in the molecular weight of polymer. This causes an increase in the bulkiness of the groups attached to the adsorption center and hence reduces the rate of corrosion [35, 36].

2.3 Recycling copolymer vinyl pyrrolidone/vinyl acetate as corrosion inhibitors

Recycled copolymer vinyl pyrrolidone/vinyl acetate (VP/VA) copolymer was used in many studies as corrosion inhibitors.

In presence of surfactant with polymers in different applications and industrials is greatly noted [37]. The presence of the polymer may be lead to change the properties of the surfactant molecules. The association between polymers and surfactants molecules has been studied by several researchers [38, 39]. Several mechanisms have been proposed to describe this association. These can be summarized as the following:

a. Association of individual surfactant monomers to the polymers chain [40].

b. Association of micelle-like aggregates of the surfactant to the polymer chain [41].

c. A combination group "a" and "b" [42].

The association of polymer-micelle can be detected by [43, 44]:

1. The change in clouding behavior of the polymer,

2. The reduction in Krafft temperature of the surfactant,

3. The decrease in aggregation number,

4. ΔH_{mic} measurements.

In the present part, we report recent studies upon the association between surfactant and recycled VP/VA copolymer and its effect on the adsorption properties of the surfactant molecules on metal surfaces. The study review consists of two major parts: the association between anionic (AS) and cationic (CS) surfactant and recycled VP/VA copolymer and the effect of the association on the adsorption properties of the surfactant molecules on the corrosion of carbon steel in acidic solution.

The conductometric measurements were used to investigate the critical micelle concentration (CMC) of ionic surfactants. The break point in the plot of conductivity versus surfactant concentration point to the CMC values of the surfactant [45].

The addition of VP/VA copolymer molecules shifts the CMC values of surfactant to lower value. Many literature data [46, 47] reveal that the reduction in CMC, points to polymer-micelle association. One of the most convincing models for polymer-surfactant association has always been the binding of surfactant molecules (S) to the polymer molecules (P) through a stepwise sequence of several chemical equilibrium [48]:

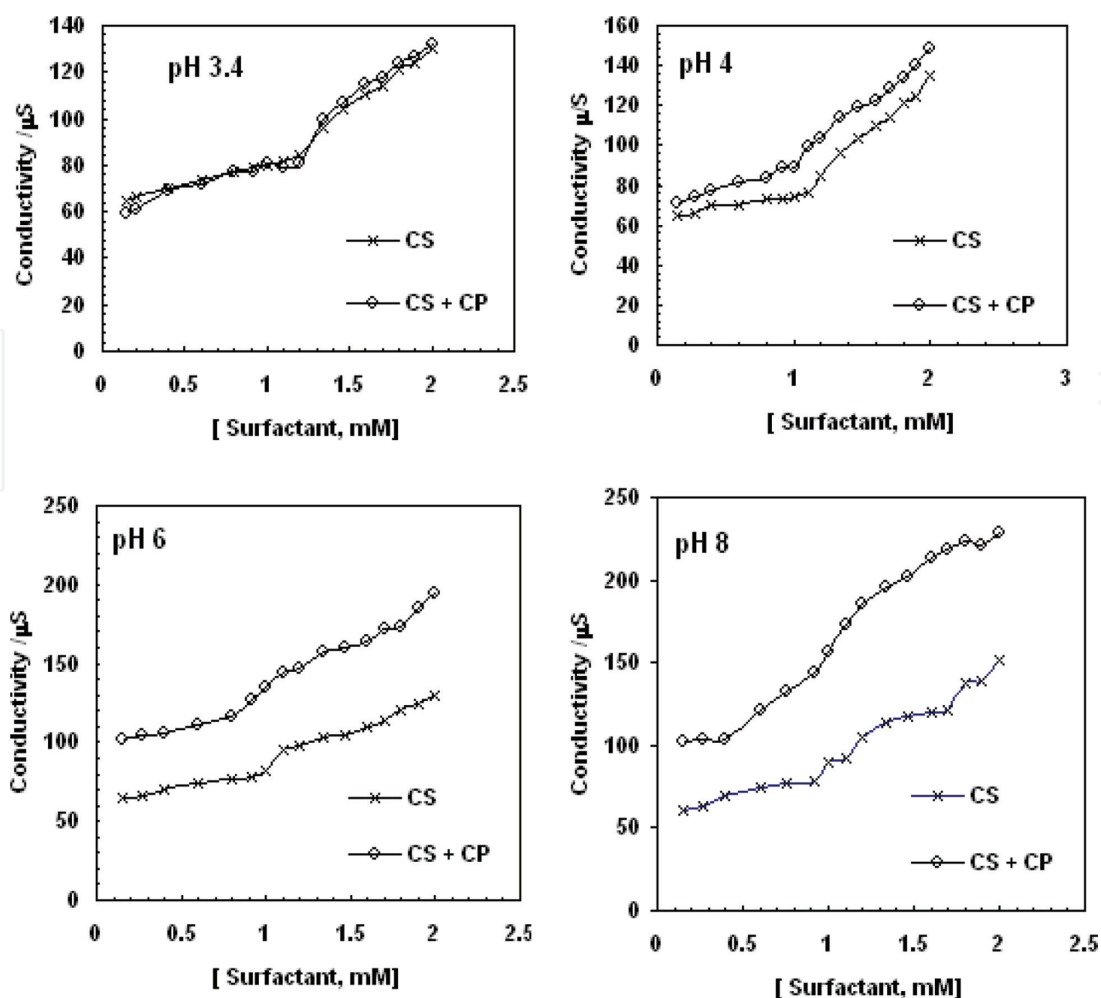$$PS_{n-1} + S \underset{K_{-n}}{\overset{K_n}{\rightleftharpoons}} PS_n \tag{2}$$

Polymer-surfactant association in solution depends on the balance forces between charge-charge interactions between surfactant head group and the dipoles of a non-ionic polymer; the hydrophobic interaction arises from water molecules and the dispersion forces between nearest-neighbor molecules [49]. On other hand, the data reveal that the presence of polymer molecule does not exert any significant influence on CMC values of cationic surfactant CS. This behavior is consistent with the fact there is no significant association comparable to CS surfactant with neutral copolymer. Many literature data suggest that the association between the surfactant and polymer are probably due to a partially positive charge transfer to the CO group of the polymer and, consequently, an increased attraction of the hydrophilic group of the anionic surfactants [49, 50]. This postulate would explain the absence or presence of very weak association between cationic surfactant and neutral copolymer.

Various factors directly influence on cationic surfactant-neutral copolymer association such as solution pH (see **Figure 3**) and additions of KCl (see **Figure 4**) to test solutions are discussed herein.

The data clearly show that in pH range for 3.4–4 there is no significant changes in CMC values of CS surfactant in the absence and presence of copolymer. On the other hand, an increase in the solution pH to 6 and 8 values will significantly increase the CMC of the CS surfactant as a result of increasing the association process. This behavior may be attributable to the increase of solution pH (in range 6–8) which leading to a reduction of the positivity of CS surfactant and, consequently, an increased attraction of the hydrophilic group of the cationic surfactant to the copolymer.

It is apparent that in the absence of KCl there are no significant changes in CMC values of CS surfactant in the absence and presence of copolymer. On other hand, addition of different KCl concentrations to CS surfactant solutions in the absence and presence of neutral copolymer decreases the CMC of the CS surfactant. This result suggests that the presence of KCl in the solutions enhances the association between CS surfactant and copolymer molecules. The extent of association increases with increasing KCl concentration form 0.02 to 0.06 mM. This behavior is due mainly to a screening effect. The clusters or pre micelles of CS surfactant which are adsorbed on the copolymer chain are surrounded by counter ions (Cl^-). As a consequence the electrical repulsion between CS surfactant and copolymer molecules is decreased and association takes place at a lower concentration of surfactant [51, 52].
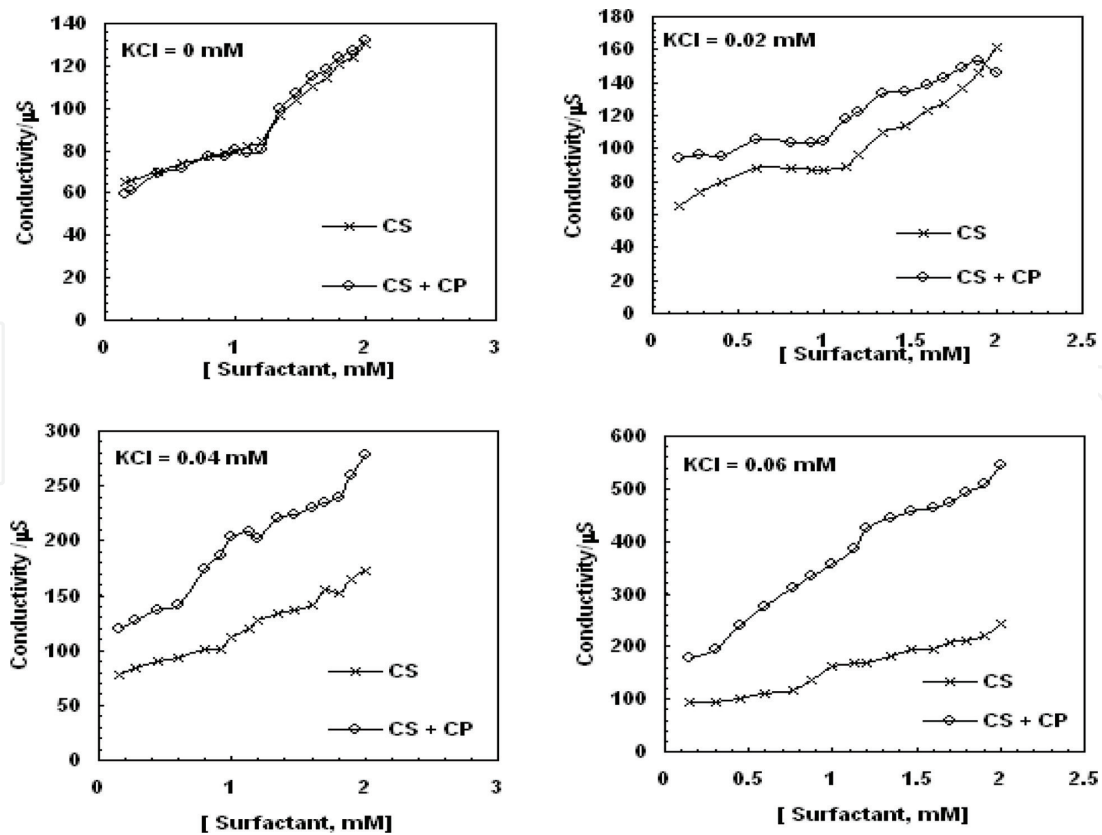
Figure 3.
Effect of solution pH on CMC values of CS surfactant.

Form the corrosion studied, it was found that the corrosion protection efficiency (P%) for the CS surfactant in the absence and presence of copolymer increased with increase in the concentration of CS until it reaches a maximum constant value corresponding to the critical micelle concentration (CMC = 0.8 mM) [53]. The protective behavior of CS may be due to adsorption of surfactant on the metal surface. The presence of 0.05 gm/l of polymer has no significant changes in protection efficiency P% and CMC values of CS surfactant. This may be suggesting that the association between CS surfactant and neutral copolymer under this condition is very week. Consequently, the corrosion inhibition of metal is mainly due to the adsorption of CS surfactant on the metal surface and formation of barrier film that separating the metal surface from the corrosive acid medium.

The corrosion protection efficiency of CS surfactant in the absence and presence of copolymer increases with increasing the pH values. Here we also observed that the effect of pH of solution on the protection efficiency of CS surfactant. This is due to the presence of copolymer enhanced the inhibition effect of CS especially in pH range 6–8. This can be explained on the basis that the partial positive charge of copolymer decreases in pH range 6–8 and, consequently, an increased attraction to the hydrophilic group of the cationic surfactant. The obtained explanation is compared with that obtained by above conductivity studies. According to this behavior, the association between CS and copolymer molecules leads to a higher degree of coverage and this, in turn, leads to an increase in protection efficiency P% at a given pH value.

The protection efficiency of CS in the absence of copolymer increases with increasing KCl concentration. This behavior can be interpreted on the basis that addition of KCl to the solution enhances the negative charge on the metal surface and this leads to

Figure 4.
Effect of KCl concentration on CMC values of CS surfactant.

an increase in adsorption of CS on the metal surface and in turn, leads to an increase in protection efficiency P% [54]. The presence of polymer molecules with Cl⁻ ions and CS is accompanied by high protection efficiency as compared with corrosive medium contains Cl⁻ ions and CS only. It is clear that the change of the protection efficiency $(P_{CS + CP}\% - P_{CS}\%)$ increase with increasing the KCl concentration. This observation can be explained on the basis that the presence of KCl increase the adsorption of CS on the metal surface as a result of increasing the negative charge on the metal surface as well as the enhancing of the association between CS and copolymer molecules because of decreasing the electrical repulsion between CS and copolymer molecules [54]. This leads to greater surface coverage, thereby giving higher inhibition efficiency.

Different types of adsorption may be considered for the adsorption of AS surfactant molecules at the metal surface: (i) electrostatic attraction between charged molecules and the charged metal, (ii) interaction of unshared electron pairs in the molecule with the metal, and (iii) a combination of the above [55, 56].

The presence of VP/VA polymer with AS surfactant increase protection efficiency of AS and this behavior may be due to polymer-surfactant association leading to a higher degree of coverage and consequently higher corrosion inhibition [57]. The protection efficiency for AS in the absence and presence of polymer increases with increase in AS concentration until it reaches a maximum constant value corresponding to its critical micelle concentration. The maximum protection efficiency of AS in the absence of polymer (65%) was achieved at 0.67 mol/dm³. On other hand the presence of polymer enhances maximum protection efficiency of AS (73%) and achieves it at lower concentration.

2.4 Recycling polystyrene (PS) as corrosion inhibitor

A survey of pervious works revealed the using of polystyrene (PS) as corrosion inhibitor in acidic media.

Shittu et al. [58] indicated in his study that an addition of PS in small quantity reduced the corrosion rate of steel in acidic solutions (HCl and H_2SO_4). Optical inspection of the steel surface under testing showed that there was formation of thin layer on the metal surface and the layer thickness increases as the polystyrene concentration increases. This PS layer isolates the steel surface from the corrosive solution.

Románszki et al. [59] they used polystyrene layers thickness (85–500 nm) as effective coating on copper and copper alloys as well as on stainless steel 304 to control the corrosion in artificial seawater.

2.5 Recycling polyurethane (PU) as corrosion inhibitor

Kumar et al. [60] had reported polyurethane tri-block co-polymer as effective inhibitor of mild steel corrosion in acidic medium. The data indicated that the PU inhibits metal corrosion by adsorbing on metal surface to form pseudo-capacitive interface. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) analyses showed that the polymers formed protective film on MS surface and shield it from direct acid attack.

Banerjee et al. [61] investigated a series of polyurethane (PU) with different degree of sulfonation (DS) as corrosion inhibitor for mild steel in acidic solution. More than 90% inhibition efficiency polyurethanes (PU) have been reported using only 20 ppm of the PU. Polyurethane (PU) inhibited the corrosion of steel through adsorption process. Surface coverage by PU has been scaled using scanning electron microscopy (SEM) and atomic force microscopy (AFM).

3. Conclusion

The recycling of polymeric waste and use of their modified products as effective corrosion inhibitors for metal corrosion are limited. In this chapter, it is intended to report a series of efforts aimed to the converting plastic waste into useful material used to control the corrosion of metal in very high corrosive environmental. Many of the reports deal with novel polymeric corrosion inhibitors in various applications were discussed in this chapter.

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